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Some Electronic and Dynamical Factors in Electron-Transfer

Chemistry: Metal Complexes, Clusters, and Surfaces

by

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SOME ELECTRONIC AND DYNAMICAL FACTORS IN ELECTRON-TRANSFER CHEMISTRY: METAL COMPLEXES, CLUSTERS, AND SURFACES

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ABSTRACT. Some selected concepts involving electronic and dynamical factors in the electron-transfer chemistry of inorganic and organometallic systems are outlined and illustrated by recent results primarily from the author's laboratory, with some emphasis placed on the redox properties of electrochemical interfaces in comparison with molecular reagents. Three interrelated topics are considered. The first concerns the control of electron-transfer rates by an interplay between donor-acceptor electronic coupling and nuclear dynamics. The role of the solvating medium in limiting the barrier-crossing frequency ("solvent friction" effects) is described, and the diagnostic capabilities (and limitations) of this phenomenon for probing the degree of electronic coupling by "tuning" the reaction dynamics are noted. Secondly, the behavioral differences anticipated between the kinetic properties of molecular redox reagents and electrode surfaces are discussed. A formalism is described for this purpose which intercompares homogeneous-phase and heterogeneous rate data on a unified basis, and is utilized in some illustrative experimental comparisons. Thirdly, the infrared spectroelectrochemical properties of high-nuclearity platinum carbonyl clusters in nonaqueous solvents are outlined in comparison with the potential-dependent properties of monocrystalline platinum electrode analogs. The results prompt a distinction between charge- and potential-dependent surface properties. The former factor controls localized surface bonding, which is apparently insensitive to the surface geometry; however, the surface charge-potential relationship (i.e. the surface capacitance) is appreciably different between the metal clusters and the planar metal interfaces.

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1. Introduction

The exploration of electron-transfer (ET) phenomena in chemistry has long been intertwined with inorganic and organometallic systems, and with

electrode surfaces, both separately and in tandem. The former emphasis arose from the early recognition that such compounds offer a rich variety of single-electron redox couples having well-defined molecular structures and widely differing thermodynamics. Besides their practical utility, these systems have been utilized extensively for testing theoretical models of electron transfer; such strong interplay between theory and experiment is a hallmark of redox chemistry in general. Aside from the well-known utilization of electrodes for evaluating redox thermodynamics, electrochemical kinetics has long been a fertile field of investigation, including heterogeneous electron transfer involving inorganic and organometallic redox couples. Perhaps surprisingly, however, research into electrochemical kinetics has tended to develop in distinctly different directions to ET kinetics in homogeneous media. The overlap between these disciplines is nevertheless naturally broad.

The aim of this conference paper is to outline selected phenomena, of recent interest to the author, that illustrate some ET properties of inorganic and organometallic systems in relation to the behavior of metal-solution interfaces themselves. Three interrelated topics will be considered. The first concerns the limitations placed on ET reaction rates by the interplay of donor-acceptor site electronic coupling and nuclear reaction dynamics, and considers the role of the solvent medium in controlling the latter factor. Secondly, an anticipated relationship between the ET kinetic properties of molecular redox reagents and metal electrode surfaces will be outlined, and the predictions compared with experimental data. A third, closely related, issue concerns comparisons between the solution-phase redox properties of large metal clusters and metal-solution interfaces, involving specifically the infrared spectroelectrochemical properties of high-nuclearity platinum carbonyls and CO-saturated monocrystalline platinum electrodes. The, we believe novel, aim here is to compare the electronic and charge-dependent coordinative properties of structurally related metal clusters and metal electrodes.

2. The Interplay of Electronic and Nuclear Dynamical Factors in Electron Transfer

An obvious requirement for effective electron transfer between a pair of redox sites, either contained within molecules (or pairs of molecules) in solution or between a molecular species and a metal surface, is the occurrence of significant overlap between the donor and acceptor molecular orbitals. Electron-transfer reactions are unique in chemistry in proceeding even when there is extremely weak ($\ll 1$ kJ mol⁻¹) interaction between the reacting centers; indeed electron transfer is believed to occur effectively over 20 - 30 Å in some systems, such as metalloproteins [1]. Nevertheless, for bimolecular reactions between conventional inorganic or organometallic species, or for electrochemical processes, the reacting centers are commonly expected to be able to approach sufficiently closely (say within 4 - 8 Å) prior to electron transfer so to yield substantial orbital overlap. In general, the influence of such electronic interactions upon the efficiency of electron transfer is



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prescribed by the so-called *electronic coupling matrix element*, H_{12} [2,3]. Even for outer-sphere reactions, i.e. where no formal chemical bond exists between the redox centers, H_{12} is anticipated to vary substantially (say from ca. 0.1 to 10 kJ mol⁻¹) for inorganic and organometallic systems [3].

The magnitude of the electronic matrix coupling element can influence the kinetics of electron transfer in two ways. First, for weak coupling (small H_{12}), the frequency of electron tunneling within the transition state (and hence the preexponential component of the rate) is given by [2]:

$$\nu_{el} = H_{12}^2 (\pi^3 / \Delta G^* h^2 k_B T)^{1/2} \quad (1)$$

where ΔG^* is the activation free energy, h is the Planck constant and k_B is the Boltzmann constant. Equation (1) displays a clear sensitivity of ν_{el} , and hence the reaction rate, to the magnitude of H_{12} . As the electronic coupling (H_{12}) is increased, however, the ET rate will eventually become limited by the frequency of passage along the nuclear reaction coordinate at the barrier top, ν_n , as prescribed by the dynamics of the various nuclear modes (reactant vibrations, solvent polarization, etc.) contributing to the activation barrier (vide infra).

More generally, then, it is useful to consider a *net barrier-crossing frequency*, $A_{et} = \kappa_{el} \nu_n$, with the *electronic transmission coefficient* κ_{el} describing the (fractional) probability of electron transfer occurring each time the system reaches the barrier top. An illustrative, albeit simplified, expression for κ_{el} is [2]:

$$\kappa_{el} = 2[1 - \exp(-\nu_{el}/2\nu_n)]/[2 - \exp(-\nu_{el}/2\nu_n)] \quad (2)$$

Two limiting cases of Eq (2) are noteworthy. Firstly, for sufficiently weak electronic coupling (i.e. small H_{12}) such that $\nu_{el} \ll \nu_n$, Eq (2) reduces to $\kappa_{el} \approx \nu_{el}/\nu_n$, so that the net preexponential factor $A_{et} = \nu_{el}$. Processes within this limit are designated as occurring via *nonadiabatic pathways*, whereupon the barrier-crossing frequency is proportional to $(H_{12})^2$, and *independent* of the nuclear dynamics (ν_n). Secondly, for sufficiently strong electronic coupling (i.e., large H_{12}) such that $\nu_{el} \gg \nu_n$, Eq (2) reduces simply to $\kappa_{el} \rightarrow 1$, so that $A_{et} \approx \nu_n$. Reactions fulfilling this condition are denoted as proceeding via *adiabatic pathways*, whereupon the barrier-crossing frequency is limited solely by the nuclear reaction dynamics.

Nevertheless, the electronic coupling can still influence the rate of such adiabatic pathways by diminishing the barrier height. A general expression for the observed rate constant of bimolecular homogeneous-phase or electrochemical reactions is [2,4,5]:

$$k_{ob} = K_p \kappa_{el} \nu_n \exp(-\Delta G^*/k_B T) \quad (3)$$

where K_p is a precursor equilibrium constant, describing the probability of finding the reactant(s) in a spatial configuration suitable for electron transfer.

To a first approximation [6], the barrier height ΔG^* is diminished below the cusp value ΔG^*_c which would apply in the absence of electronic coupling, by

$$\Delta G^* = \Delta G^*_c - H_{12} \quad (4)$$

Consequently, then, reaction rates are generally anticipated to be sensitive to the nature of the donor-acceptor electronic coupling.

For intramolecular ET reactions having relatively strong electronic coupling, H_{12} can be evaluated experimentally in suitable cases from the intensity of the near-infrared optical ET transition [9]. For most homogeneous-phase outer-sphere, or electrochemical reactions, however, such direct assessments of H_{12} are unavailable. Nonetheless, as already mentioned, a distinct behavioral difference between nonadiabatic and adiabatic ET processes is that the rates for the latter, but not the former, should be sensitive to the nuclear dynamics as embodied in ν_n . Provided that some means is available by which ν_n can be altered systematically, an experimental distinction between adiabatic and nonadiabatic pathways, and perhaps the diagnosis of intermediate cases, might be forged from the sensitivity of k_{ob} to ν_n . While certainly not straightforward, an interesting tactic along these lines has recently become apparent from considerations of dynamical solvent effects on ET processes. Since we have recently reviewed this overall topic in detail elsewhere [10], only a brief discussion of some pertinent points is given here.

The solvent has long been known to exert important influences upon the activation barrier to electron transfer; such *energetic* factors form a mainstay of the classic theoretical treatments due to Marcus and others. Over the last ten years or so, it has become apparent that ET rates can also be affected importantly by the solvent *dynamical* properties. In essence, the frequency of net progress along the reaction coordinate for an ET barrier composed primarily of outer-shell (solvent) reorganization is often predicted to be dominated by so-called *overdamped* solvent motion, associated with the collective repolarization of solvent dipoles necessary to reach the transition state and hence consummate electron transfer. The notion of "overdamped" dynamics refers to the commonly anticipated situation where the motion of individual dipoles is impeded by irreversible energy transfer to surrounding molecules (dissipative relaxation), so that the *net* solvent repolarization dynamics as described by an effective dielectric relaxation time, τ_{eff} , can be considerably slower than that for rotation of individual solvent dipoles, τ_{rot} . This situation, where $\tau_{eff} < \tau_{rot}$, corresponds to a breakdown of conventional transition-state theory (TST), and provides a number of interesting ramifications [11].

For the present purposes, it is sufficient to note that τ_{eff} in a number of simple polar solvents can be approximated by the *longitudinal relaxation time*, τ_L , extracted from solvent dielectric loss spectra. Interestingly, substantial (up to ca 50 fold) variations in τ_L are observed in such media, from ca. 0.25 to 10 ps [12]. Since analytic theories predict commonly that $\nu_n \sim \tau_L^{-1}$, correspondingly large variations in ν_n are anticipated to be achieved by suitable alterations in

the solvent medium. The apparent ability to "tune" the nuclear dynamics in this manner is clearly of substantial value.

A complication, however, is that changing the solvent medium will generally alter the reaction energetics (ΔG^*) as well as dynamics. The former effect can be especially large for energetically nonsymmetric reactions, since the driving force ΔG° is then usually solvent dependent. A simpler situation applies to electron exchange processes, for which $\Delta G^\circ = 0$, since ΔG^* will now equal (aside from work terms) the *intrinsic barrier* ΔG^*_{int} . The solvent dependence of the latter can be predicted to a first approximation from dielectric-continuum theory. A substantial number of studies of both electrochemical exchange and homogeneous self-exchange reactions in various solvents have been published since 1985, with solvent-dependent kinetic analyses aimed at unraveling the sensitivity of the rate constant for electron exchange, k_{ex} , to the solvent dynamics [10]. The usual strategies involved are embodied conveniently in the relation:

$$\log k_{\text{ex}} = \log \kappa_{\text{el}} \nu_n + \log K_p - C(\epsilon_{\text{op}}^{-1} - \epsilon_0^{-1}) \quad (5)$$

This equation follows from Eq (3) by assuming that ΔG^* equals the outer-shell intrinsic barrier as predicted by the usual dielectric-continuum model, contained in the last term in Eq (5); ϵ_{op} and ϵ_0 are the solvent optical and zero-frequency (i.e. static) dielectric constants, respectively, and C is a constant that depends on the precursor-state geometry.

Provided that K_p is indeed solvent insensitive, distinctly different solvent dependencies of k_{ex} can often be anticipated from Eq (5) for reactions following largely adiabatic and nonadiabatic pathways [10]. In the latter case, as noted above the preexponential term $\kappa_{\text{el}} \nu_n$ will be independent of ν_n and hence the solvent dynamics, so that $\log k_{\text{ex}}$ should correlate with $(\epsilon_{\text{op}}^{-1} - \epsilon_0^{-1})$. On the other hand, substantial departures from this behavior should be seen for adiabatic pathways since $\kappa_{\text{el}} \nu_n$ can then be strongly solvent dependent. For polar Debye solvents, $\log \tau_L^{-1}$ tends to increase along with $(\epsilon_{\text{op}}^{-1} - \epsilon_0^{-1})$; this correlation can yield $\log k_{\text{ex}} - (\epsilon_{\text{op}}^{-1} - \epsilon_0^{-1})$ slopes of *opposite sign* to those anticipated for nonadiabatic processes. Illustrative examples of reactions following both limiting cases have been described [13]. Several other related solvent-dependent analyses have been discussed [10b,14,15]. All are limited in various ways by the assumed applicability of the dielectric-continuum model of the reaction energetics and dynamics, and are therefore valid at best only on a semiquantitative level [10b].

In a few cases, however, a more quantitative analysis can be undertaken whereby the desired solvent-dependent ΔG^*_{int} values are obtained experimentally from optical ET reorganization energies for related binuclear systems. An example of this approach, involving self exchanges of metallocenium-metallocene ($\text{Cp}_2\text{M}^{+/0}$) redox couples in various polar Debye solvents is worth highlighting here since ET rate-solvent dependencies are observed that span the limits of nonadiabatic and adiabatic behavior [12]. For ferrocenium-ferrocene couples, the rate constants k'_{ex} (corrected for ΔG^* -solvent variations) are almost independent of the solvent dynamics, as

discerned by τ_L^{-1} . For the more facile cobaltocenium-cobaltocene couples, $\log k'_{ex}$ is seen to be significantly dependent upon $\log \tau_L^{-1}$; for the fastest systems, the $\log k'_{ex} - \log \tau_L^{-1}$ slope approaches unity towards smaller τ_L^{-1} values, as expected for adiabatic pathways. By comparing this spectrum of $k'_{ex} - \tau_L^{-1}$ behavior with corresponding plots calculated for different degrees of electronic coupling, approximate estimates of H_{12} could be obtained [12]. These values, varying between ca. 0.4 and 5 kJ mol⁻¹, are in approximate agreement with theoretical H_{12} estimates (for $Cp_2Fe^{+/0}$ and $Cp_2Co^{+/0}$) [3,16]. The greater electronic coupling obtained for cobaltocenes versus ferrocenes can be understood qualitatively in terms of the ligand- and metal-centered molecular orbitals, respectively, involved in these ET processes [17].

This sensitivity of the $\log k'_{ex} - \log \tau_L^{-1}$ dependence, as well as the ET self-exchange rates themselves, to the metallocene electronic structure is in contrast to the electrochemical exchange kinetics, which exhibit similarly facile rates with $k_{ex} - \tau_L^{-1}$ dependencies indicating the presence of largely adiabatic pathways [17,18]. Indeed, the large majority of electrochemical exchange processes subjected to solvent-dependent analyses exhibit $k_{ex} - \tau_L^{-1}$ behavior consistent with the occurrence of adiabatic pathways, although exceptions have been noted [13]. This suggests that even outer-sphere electrochemical processes commonly proceed via pathways involving at least moderate electronic coupling (say, ≥ 2 kJ mol⁻¹). While consistent with some theoretical expectations, such apparent dependencies of the ET rates on the solvent dynamics, however, can also result from experimental artifacts [10b].

Finally, it is worth noting that the nature of the solvent-dependent ET dynamics is also predicted to be affected by the presence of inner-shell (reactant vibrational) contributions to the activation barrier [19]. As might be expected, the presence of higher-frequency vibrational contributions to the activation barrier can yield a marked attenuation in the degree to which overdamped solvent dynamics control the adiabatic barrier-crossing frequency [19]. The experimental exploration of such effects is limited in part by the paucity of redox couples suitable for solvent-dependent studies that exhibit known vibrational barriers, and complicated by the qualitatively similar behavior expected for nonadiabatic pathways. Nevertheless, there is some evidence that vibrational activation can indeed attenuate the role of solvent dynamics, although the theoretical predictions appear to overestimate the magnitude of this effect [10b,20].

3. Kinetic Properties of Metal Electrodes versus Molecular Redox Reagents

A fundamental topic in electron-transfer chemistry involves understanding reaction rates in terms of the intrinsic, as distinct from thermodynamic, properties of the redox couples involved, and the environment in which the reaction occurs. The intercomparison of homogeneous-phase rates involving related pairs of redox couples by means of treatments based on Marcus theory is well known, especially in inorganic chemistry [2]. An equally intriguing, but

less extensively explored, issue of this type involves comparisons of the kinetics of related electrochemical and homogeneous-phase reactions. The most well-known formula for this purpose, based on Marcus theory, relates the rate constants for corresponding electrochemical exchange and homogeneous self exchange processes, k_{ex}^e and k_{ex}^h , respectively, by [21].

$$k_{ex}^e/A^e \approx (k_{ex}^h/A^h)^{1/2} \quad (6)$$

where A^e and A^h are the appropriate overall preexponential factors. An additional, perhaps more useful, equation relates electrochemical rate constants, k_1^e and k_2^e , for a pair of reactions at the same electrode potential, E , with the homogeneous-phase rate constants for the same two redox couples, k_1^h and k_2^h , reacting with a common reagent R [21]:

$$(k_1^e/k_2^e)_E = (k_1^h/k_2^h)_R \quad (7)$$

This latter relation is applicable to chemically irreversible as well as reversible processes.

While these relationships can be valuable for collating data and for understanding as well as predicting kinetic trends, it is enlightening to consider more specifically the manner in which the ET properties of metal surfaces can be compared with molecular (i.e. solution-phase) redox reagents. The following is extracted from a recent discussion by the present author [22]. For this purpose, it is useful to regard electrochemical (metal-solution) interfaces as a special type of redox reagent, having a continuously variable redox potential (i.e. the electrode potential, E), and which requires no nuclear reorganization to transfer the electron(s). By contrast, molecular redox reagents have a fixed redox potential (E°) under a given set of chemical and physical conditions. Electron transfer requires some nuclear reorganization associated with the surrounding solvent and often additionally from alterations in reactant bond distances (inner-shell activation) associated with the change in ionic charge. On this basis, then, one would expect electrode surfaces to commonly yield more facile ET reaction pathways than those provided by molecular redox reagents under the same thermodynamic conditions.

The order to compare directly the rates of corresponding electrochemical and homogeneous-phase processes along these lines, it is first necessary to make allowance for the difference in rate units, cm s^{-1} and $\text{M}^{-1} \text{s}^{-1}$, respectively, for these two types of reaction, arising from the two- and three-dimensional nature of the reaction environments. A simple means of achieving this entails shrinking (hypothetically) the metal electrode radius from infinity (i.e. a plane surface) down to a sphere of a same size as the molecular reagent without altering its properties. This allows electrochemical rate constants, $k^e(\text{cm s}^{-1})$, to be transformed into "equivalent second-order" rate constants, $k^{e2}(\text{M}^{-1} \text{s}^{-1})$, that would be observed if the metal surface offered the same geometric environment to the reactant as the molecular reagent. The required transformation from linear to spherical coordinates is

$$k^{e2} = 4\pi N r_h^2 k^e \quad (8)$$

where N is Avogadro's number and r_h is the radius of the molecular reagent [22].

The comparison between k^{e2} and the corresponding rate constant, k^h , for reduction (or oxidation) of the same species by a molecular reagent is most straightforward when the former is evaluated at an electrode potential equal to the standard (or formal) potential for the latter reagent, since the thermodynamic (driving force) terms thereby approximately cancel. Under these conditions, and in the specific cases where: (a) the inner-shell barrier associated with the molecular reagent ($\Delta G^*_{i,h2}$) is negligible and (b) in the absence of stabilizing reactant-electrode image interactions, we expect that:

$$k^{e2} = k^h (\kappa^e_{el} \delta r_e / \kappa^h_{el} \delta r_h) \quad (9)$$

Here κ^e_{el} and κ^h_{el} are the electronic transmission coefficients associated with the electrochemical and homogeneous reagent pathways, and δr_e and δr_h are the corresponding "reaction-zone thickness"; i.e., the range of inter-reactant distances within the precursor states that contributes effectively to the observed reaction rate. When assumption (a) above does not apply, i.e. when the molecular reagent contributes a significant inner-shell barrier, the observed rate constants k^{h2} can be corrected readily for this effect if $\Delta G^*_{i,h2}$ can be calculated, yielding "inner-shell corrected" rate constants k^{h2} . Fortunately, $\Delta G^*_{i,h2}$ for many redox reagents is small and/or can be estimated reliably.

Comparisons between corresponding k^{e2} and k^{h2} values obtained in this manner can yield interesting insights into electrochemical versus homogeneous-phase ET reactivity [22]. Table I contains an abbreviated illustration of some reactivity comparisons along these lines, taken from ref. 22. Three types of comparative reactions are represented, all referring to one-electron electroreductions at mercury electrodes. The first variant (entries 1 - 5) involves the outer-sphere reductions of cationic transition-metal complexes by $\text{Ru}(\text{NH}_3)_6^{2+}$ in aqueous media. This reductant is of particular interest since it obliges the reactions to follow outer-sphere ET pathways. The penultimate right-hand column lists the "equivalent second-order" electrochemical rate contents, k^{e2} , obtained from the work-corrected values measured at the formal potential, $E_f = -0.185$ V vs SCE, for the reducing agent $\text{Ru}(\text{NH}_3)_6^{2+}$, by means of Eq (8). The far right-hand column contains corresponding work-corrected rate constants for the homogeneous-phase reduction by $\text{Ru}(\text{NH}_3)_6^{2+}$, corrected for the small (1.5 kJ mol^{-1}) inner-shell barrier contributed by this reductant (see ref. 22 for details).

Comparison between these corresponding k^{e2} and k^{h2} values in Table I shows that uniformly $k^{e2} > k^{h2}$, the electrochemical rates ranging between ca $10 - 10^3$ fold faster than the homogeneous-phase values. The largest inequalities are seen for the metal ammine reductions. As discussed in ref. 22, the origins of these notably higher reactivities in the electrochemical environment probably lie at least partly in the greater efficiency of electron tunneling for the electro-

TABLE I Illustrative Comparison between "Equivalent Second-Order" Rate Constants for One-Electron Reductions at Mercury Electrodes and Rate Constants involving Homogeneous-Phase Molecular Reagents (abstracted from ref. 22)

No.	Oxidant	Reductant	Environment ^a	$k^e b$ cm s ⁻¹	k^{e2c} M ⁻¹ s ⁻¹	k^{h2d} M ⁻¹ s ⁻¹
1	Co(NH ₃) ₆ ³⁺	Ru(NH ₃) ₆ ²⁺	Aqueous	4x10 ⁻⁵	1.3x10 ³	0.45
2	Co(NH ₃) ₅ F ²⁺	Ru(NH ₃) ₆ ²⁺	"	6x10 ⁻⁵	2.0x10 ³	2.7
3	Ru(NH ₃) ₆ ³⁺	Ru(NH ₃) ₆ ²⁺	"	2.5	8.5x10 ⁷	3.5x10 ⁵
4	Fe(OH ₂) ₆ ³⁺	Ru(NH ₃) ₆ ²⁺	"	~5	1.7x10 ⁸	2.7x10 ⁷
5	V(OH ₂) ₆ ³⁺	Ru(NH ₃) ₆ ²⁺	"	5.5x10 ⁻⁷	20	1.4
6	O ₂	Ru(NH ₃) ₆ ²⁺	"	0.06	2.0x10 ⁶	1.1x10 ²
7	Cp ₂ Co ⁺	Cp ₂ Co	DMF	2.0	9x10 ⁷	7x10 ⁷
8	Cp ₂ Co ⁺	Cp ₂ Co	TMU	0.35	1.5x10 ⁷	3.5x10 ⁷

^aRu(NH₃)₆²⁺ reductions refer to aqueous media; Cp₂Co reductions (Cp=cyclopentadienyl) refer to dimethylformamide (DMF) and tetramethylurea (TMU) solvents, as indicated.

^bWork-corrected rate constant for reduction at mercury electrode, at electrode potential equal to E_r of reductant [-0.185 V vs SCE for Ru(NH₃)₆^{3+/2+}] (see ref. 22 for data sources, etc).

^c"Equivalent second-order rate constant" for electrochemical reduction, obtained from k^e value in adjacent column by using Eq (8) (see ref. 22).

^dWork-corrected rate constant for corresponding reduction by homogeneous-phase reducing agent, also corrected for inner-shell barrier contribution from the reductant (see ref. 22 for data sources)

chemical versus the homogeneous-phase processes, i.e., ($\kappa^e_e \delta r_e / \kappa^h_e \delta r_h$) \gg 1 in Eq (9). Thus evidence has been marshalled to indicate that at least the Co(III) ammine-Ru(NH₃)₆²⁺ reactions are strongly nonadiabatic [23], whereas the Co(III) ammine and (to a lesser extent) the metal aquo electroreductions appear to follow largely adiabatic pathways [24]. The latter is consistent with the close approach of metal ammine reactants to the metal surface deduced on the basis of the sensitivity of the ET rates to variations in the double-layer potential profile [25]. An additional factor favouring the electrochemical

processes may be the presence of stabilizing reactant-electrode image interactions, which are not considered in Eq (9). Evidence against at least the predominant importance of this factor, however, can be gleaned on both experimental and theoretical grounds, as outlined in ref. 22.

The second type of reaction in Table I, represented by entry 6, concerns the irreversible reduction of a non-metal species, dioxygen. Comparison of the k^{e2} and k^{h2} values shows again that the former is substantially faster, by 2×10^4 fold. This result is of significance since it demonstrates that a reaction pathway for dioxygen reduction that is notably more facile than those engendered by the outer-sphere reductant $\text{Ru}(\text{NH}_3)_6^{2+}$ can be engendered even at the relatively "noncatalytic" mercury-aqueous interface. Such a rate acceleration may again be due partly to greater electronic coupling, but appears more likely to result from specific solvation and other short-range environmental factors [22].

The last type of example in Table I, entries 7 and 8, concerns $\text{Cp}_2\text{Co}^{+/0}$ electron exchange in a pair of solvents, dimethylformamide (DMF) and tetramethylurea (TMU). These media were selected since they offer significantly different overdamped solvent dynamics, with τ_L^{-1} values of 7.5×10^{11} and $1.7 \times 10^{11} \text{ s}^{-1}$, respectively. This type of reaction is included partly to emphasize that the present treatment is applicable to electron-exchange, as well as nonsymmetric ET processes. In the former case, one merely compares directly rate data for electrochemical exchange and homogeneous self-exchange since the former necessarily refers to an electrode potential equalling E_f for the molecular reductant (or oxidant). In contrast to the above examples, both the corresponding k^{e2} and k^{h2} values are seen to be closely similar, within ca. twofold of each other. It therefore appears that the electrochemical and homogeneous-phase reductants offer similarly facile reaction environments in this case. Given the discussion in the last section, it is worth noting that the variation in k^{e2} with τ_L^{-1} is distinctly greater than that observed for k^{h2} (Table I). This difference, which is observed more generally, most likely reflects the occurrence of stronger electronic coupling at the metal surface than for the homogeneous-phase bimolecular process, thereby yielding a larger dependence of the ET rate on the solvent dynamics, as expected for a more adiabatic pathway.

4. Charge-Dependent Spectroelectrochemical Properties of High-Nuclearity Pt Carbonyl Clusters in relation to Pt-CO Electrodes

Such behavioral differences between the redox properties of metal surface and metal complex reagents raises the more general issue of the manner in which the electronic nature of electrode surfaces might usefully be intercompared with molecular solutes. It has long been recognized that metal clusters represent a state of matter that, being intermediate between small metal complexes and metal surfaces, enable the differences between the chemistry of such systems to be bridged in an experimental fashion [26]. Besides the preparation and examination of naked metal clusters in the gas phase, which

has attracted considerable recent attention [27], a variety of ligand-stabilized metal clusters have been synthesized and structurally characterized, especially in the solid state [28]. Nevertheless, there has been surprisingly little attention devoted so far to the electrochemical redox properties of the latter systems. In particular, one might anticipate that larger solution-soluble clusters would exhibit a rich redox chemistry as a result of the ready availability of unfilled low-lying molecular orbitals.

In collaboration with the group of L. F. Dahl (University of Wisconsin-Madison), we have recently explored the infrared spectroelectrochemical properties of several high-nuclearity platinum carbonyl clusters in nonaqueous media [29-31]. The dianions $[\text{Pt}_{24}(\text{CO})_{30}]^{2-}$, $[\text{Pt}_{26}(\text{CO})_{32}]^{2-}$, and $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ have previously undergone detailed x-ray structural examination by Dahl *et al.*; they feature hexagonal close-packed "surface facets" with CO coordinated in both terminal and twofold bridging geometries in an analogous fashion to monocrystalline platinum surfaces [28]. Intriguingly, all three Pt clusters exhibit a rich sequence of reversible redox transitions involving net charges, n , from 0 to -10 [29,30]. For $[\text{Pt}_{24}(\text{CO})_{30}]^n$ and $[\text{Pt}_{38}(\text{CO})_{44}]^n$, uniformly one-electron voltammetric steps are observed, although the electrode-potential regions over which the odd-charge states are stable (i.e. the spacings between successive E_f values) are markedly smaller than for the even-charge states. Indeed, for $[\text{Pt}_{26}(\text{CO})_{32}]^n$ two-electron steps involving even-charge states are chiefly observed. The clusters therefore provide effectively "solubilized microscopic chunks" of Pt metal that can be charged progressively more negative in a fashion closely akin to Pt electrodes at potentials negative of the potential of zero charge (pzc) [30].

Moreover, infrared spectroelectrochemistry shows that the C-O stretching frequencies for the binding and especially the terminal (ν_{CO}^t) coordinated ligands decrease systematically as n becomes more negative; for example, ν_{CO}^t for $[\text{Pt}_{24}(\text{CO})_{30}]^n$ diminishes by 15 - 20 cm^{-1} per added electron. These ν_{CO}^t frequency-cluster charge dependencies are closely analogous to the corresponding ν_{CO} frequency-potential dependencies commonly observed for CO adlayers at platinum electrodes, including monocrystalline surfaces in aqueous and nonaqueous media under similar conditions (electrode potentials, solvents) as for the metal clusters [32,33]. These latter ν_{CO} frequency-electrode potential dependencies are usually ascribed to increased $\text{dn}(\text{Pt}) \rightarrow 2\pi^*(\text{CO})$ backbonding as the surface charge becomes more negative, or to a first-order Stark (electric field) effect [34].

Two related comparisons between these charge-dependent metal-cluster and analogous metal-surface properties [30] are worth noting specifically here. The first involves examining the effective ν_{CO}^t - E slopes (commonly, if imprecisely, termed "Stark-tuning rates") for corresponding Pt cluster-solvent and Pt electrode/CO-solvent interfaces. While the surface charge-potential behavior is necessarily quantized for the former systems, approximate ν_{CO}^t - E slopes can nonetheless be extracted from the changes in ν_{CO}^t brought about over a potential span which is sufficiently large (say 2 V) so to encompass several sequential redox steps. Significantly, the ν_{CO}^t - E slopes observed for the

clusters, ca $40 - 50 \text{ cm}^{-1}\text{V}^{-1}$, are significantly (2 - 4 fold) larger than those obtained for the corresponding Pt(111)/CO-nonaqueous interfaces.

These differences were found to be due chiefly to larger "effective surface" capacitances (i.e. charge- E_f dependencies) for the cluster solutes than for the electrode-solution interfaces. By estimating the surface area of the clusters, approximate values of the effective cluster surface capacitance, $C_s \approx 15 - 20 \mu\text{F cm}^{-2}$, were obtained. These values are significantly higher than those measured for the corresponding Pt(111)/CO- and Pt(110)/CO-acetonitrile interfaces, $6(\pm 1)\mu\text{F cm}^{-2}$ [30]. Such differing capacitances for effectively spherical and planar conducting surfaces can be accounted for largely by simple geometric electrostatic considerations [30]. This finding is noteworthy: given that stepwise cluster reduction results in a progressive filling of molecular orbitals, the increasing energies of these orbitals might be expected to yield lower effective C_s values in comparison with metal surfaces which feature an energetically continuous electronic band structure.

One possible point of confusion regarding the notion of "cluster surface capacitance" is also worthy of comment here. For electrode surfaces, capacitance charging is usually denoted as a nonfaradaic process to distinguish it from faradaic events that involve necessarily electron transfer across the metal-solution interface. From the cluster solutes, however, all charge build-up must necessarily occur via electron transfer from a source present in, or in contact with, the same solution (such as the gold electrode utilized in the spectroelectrochemical measurements). Of course, charging of plane metal surfaces may also occur by this faradaic mechanism, but is more conveniently achieved by connection to an external electrical source, thereby acting as a polarizable electrode.

The second comparison of note here concerns examining instead the dependence of ν_{CO}^t on the electronic charge *per surface Pt atom*, σ_{Pt} ("surface charge density"). Significantly, when examined in this manner all the cluster-solvent systems yield almost coincident linear $\nu_{\text{CO}}^t - \sigma_{\text{Pt}}$ plots, with a slope of $400 (\pm 20) \text{ cm}^{-1} (e^- \text{ per Pt atom})^{-1}$ and an intercept close to 2080 cm^{-1} . A similar $\nu_{\text{CO}}^t - \sigma_{\text{Pt}}$ dependence was also extracted for the Pt(111)/CO-acetonitrile interface from the combined $\nu_{\text{CO}}^t - E$ and surface capacitance data. This remarkably uniform $\nu_{\text{CO}}^t - \sigma_{\text{Pt}}$ behavior infers that the Pt-CO surface bonding has a localized character in that it is dependent largely on the local (albeit averaged) electron density rather on the longer-range potential distribution. For a given surface charge density, the latter quantity is markedly dependent on the geometry of the metal-solvent interface, accounting for the appreciably larger $\nu_{\text{CO}}^t - E$ (and $\sigma_{\text{Pt}} - E$) dependencies observed for the microscopically spherical clusters in comparison with the planar electrodes.

An interesting consequence of these combined effects is that remarkably large negative surface charge densities can be established on the Pt clusters. Thus the $[\text{Pt}_{26}(\text{CO})_{32}]^{10-}$ state, formed by a final two-electron reduction at -2.3 V (vs. ferrocenium-ferrocene) in acetonitrile, corresponds to a σ_{Pt} value of nearly $0.5 e^-$ per surface Pt atom. Such charge densities are markedly higher than can generally be achieved on planar electrode surfaces, for which usually $\sigma_{\text{M}} \leq 0.1 e^-$ per surface metal atom. While larger σ_{M} values could in principle be

established, solvent reduction (or oxidation) commonly acts to limit the degree of electrode charging (i.e. polarization).

Overall, then, the examination of metal cluster electrochemistry (and spectroelectrochemistry) can offer useful insight into the electronic properties of such molecular solutes in relation to electrochemical interfaces in addition to the fundamental features of the clusters themselves. Recalling the foregoing discussion, it would clearly be of interest to compare the electron-transfer *kinetic* properties of such high-nuclearity metal clusters in comparison with both small molecule (mononuclear) redox reagents and with metal electrodes. Considerations paralleling those noted here for the platinum carbonyl clusters could also be developed, for example, for the fullerenes given their similarly rich electrochemical properties [35]. In general, therefore, exploration of the relationships between the redox properties of interfacial electrochemical and homogeneous molecular-based systems promises to become an increasingly broadbased, as well as enticing, endeavour in the future.

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